

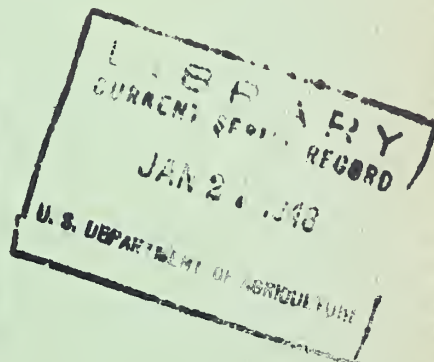
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LAKE STATES ASPEN REPORT NO. 18

CHEMICAL UTILIZATION OF ASPEN

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FOREWORD

During and since World War II, there has been increasing interest in aspen (Populus tremuloides) in the Lake States, its availability and supply, properties and uses, and management. Aspen is a tree of primary importance in 20 million acres or 40 percent of the total forest area of the three Lake States - Michigan, Minnesota, and Wisconsin.

At an informal meeting at Madison, Wisconsin, in January, 1947, forestry representatives of several federal, state, and industrial groups in the Lake States agreed that it would be desirable to bring up to date what is known on aspen and make it available to anyone interested. The job of preparing this information in the form of reports was assigned to each of the groups listed below. The reports will be duplicated as rapidly as completed, and the entire project should be finished by the end of 1947. Each report will concern one aspect of the subject. Copies will be available from the Lake States Forest Experiment Station or from each contributor.

<u>Report Number</u>	<u>Subject</u>
1	Aspen Properties and Uses
2	Aspen Availability and Supply
3	Logging Methods and Peeling of Aspen
4	Milling of Aspen into Lumber
5	Seasoning of Aspen
6	Aspen Lumber Grades and Characteristics
7	Mechanical Properties of Aspen
8	Machining and Related Properties of Aspen
9	Aspen Lumber for Building Purposes
10	Aspen for Containers
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12	Small Dimension and Other Industrial Uses of Aspen
13	Aspen for Veneer
14	Aspen for Pulp and Paper
15	Aspen for Cabin Logs
16	Aspen for Excelsior
17	Aspen Defiberization and Refining of Product
18	Chemical Utilization of Aspen
19	Preservative Treatment of Aspen
20	Marketing of Aspen
21	Possibilities of Managing Aspen

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CHEMICAL UTILIZATION OF ASPEN

PART I: WOOD

By

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Introduction

Chemical utilization of raw materials depends largely on the chemical composition and the chemical and physical properties of the raw materials under consideration. The utilization of wood is no exception to this principle. Thus, a wood having a low percentage of cellulose is uneconomical as a source of wood sugar or pulp for paper; and one of an excessively knotty character is undesirable for chemical conversion. Woods having several undesirable characteristics generally fall within the classification of species little used for the purpose. Fortunately, aspen falls outside this class.

Chemical Composition of Aspen Wood

The chemical composition of sound aspen is similar in most respects to that of several hardwoods, among which are yellow birch and sugar maple. Analytical data on the chemical composition of the three woods are recorded in table 1 and will be considered briefly as a means of comparing aspen with the other two woods, also indigenous to the Lake States. So far as the analytical values are concerned, quaking aspen compares favorably with yellow birch and sugar maple.

Extractives

Extractives are designated as materials soluble in neutral solvents, such as water, alcohol, alcohol-benzene mixtures, and ether. They form no part of the wood structure. A cursory examination of the analytical values recorded in table 1 suggests that, so far as extractives are concerned, nothing extraordinary on a quantitative basis is derivable from aspen or the other two woods. Extractives from aspen have received no serious commercial consideration. They are divided into four classes, cold-water, hot-water, alcohol-benzene, and ether extractives.

^{1/} Maintained by the U. S. Department of Agriculture, Forest Service, in cooperation with the University of Wisconsin, Madison, Wisconsin.

Table 1.--Analysis of woods (percentages based on weight of oven-dry wood)

Wood	Ash	Extractives soluble in				Acetyl	Methoxyl	Pentosans	Lignin	Holo-cellulose	Cross and Bevan cellulose	Alpha cellulose
		Cold water	Hot water	Alcohol benzene	Ether							
	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent	Per-cent
Quaking aspen	0.30	1.00	2.00	1.52	1.00	5.10	5.31	22.50	17.3	79.50	63.50	51.0
Yellow birch	.40	1.00	1.28	1.40	.31	7.42	5.90	26.86	19.3	77.00	58.75	49.7
Sugar maple	.42	.68	1.12	1.24	.45	5.52	6.40	22.81	22.3	75.20	60.40	50.0

Cold-water extractives constitute 1.50 percent of aspen as compared with 1.00 and 0.68 percent from yellow birch and sugar maple, respectively. In general, these extractives comprise sugars, gums, salts, and also tannins if present in the wood. Hot-water extractives in aspen make up 2.00 percent of the wood as compared with 1.28 and 1.12 percent in birch and maple, respectively. These extractives comprise sugars, gums, tannins, and starches. Alcohol-benzene extractives from aspen are equivalent to 1.52 percent as compared with 1.40 and 1.24 percent from birch and maple. They comprise oils, fats, fatty acids, waxes, sterols, and also some tannins, if present, from hardwoods, with the additions of resins and terpenes from softwoods. Ether extractives comprise 1.00 percent of aspen as compared with 0.31 and 0.40 percent from birch and maple, respectively. They are composed of oils, fats, fatty acids, waxes, and sterols from hardwood, with the addition of resins and terpenes from softwoods.

Minor Chemical Groups

Acetyl constitutes 5.1 percent of aspen as compared with 7.4 and 5.5 percent, respectively, in birch and maple. It is also designated as a substituent chemical group of the wood hemicelluloses with which it is combined as an ester. Acetyl, on hydrolysis, as in sulfite semi-chemical production of pulp, is converted to acetic acid. The acid is used in numerous commercial operations, such as the manufacture of rayon, plastics, solvents, adhesives, artificial leather, and curing and flavoring of foods. Methoxyl constitutes 5.3 percent of aspen as compared with 5.9 and 6.4 percent in birch and maple, respectively. It is associated with both the lignin and the hemicelluloses in the form of an ether. When removed by hydrolysis, methoxyl forms methanol (wood alcohol). In the destructive distillation of wood, one-fourth to one-third of the methoxyl is converted to methanol, the remainder being destroyed during the operation. Methanol is employed as a solvent and in the manufacture of plastics, rayons, airplane dopes, ethers, adhesives, and other materials.

Wood Constituents

Pentosans constitute 22.5 percent of aspen, 26.8 percent of birch, and 22.8 percent of maple. On hydrolysis, pentosans are converted to pentose or 5-carbon sugars known as xylose or arabinose, depending on the constitutional configuration of the pentosans. On treatment with mineral acids under specified conditions, pentosans are converted to furfural, which is employed extensively in the refining of wood rosin and petroleum oils and in the manufacture of plastics and rayons. The pentose sugars are unfermentable to ethanol by the conventional types of yeasts; only the hexose sugars are fermented to alcohol.

Lignin constitutes 17.3 percent of aspen. This value is low compared with 19.3 and 22.3 percent respectively from yellow birch and sugar maple. Lignin is the principal material that holds the fibers of the wood together, only a small percentage of hemicellulose material functioning similarly. Since aspen has a low percentage of lignin, it

is an excellent raw material for chemical wood pulps from the standpoint of low chemical requirement for the pulping operation.

The chemical requirement for pulping of wood varies with the percentage of lignin in the wood. On the weight basis, the chemical requirements for pulping aspen would be approximately 17/19 and 17/22 of that required for yellow birch and sugar maple, respectively.

Lignin in general is considered a waste product in the manufacture of chemical fibers for paper. In the sulfite pulping process it passes into the streams as a wood waste. Since aspen contains a low percentage of lignin, it is less an offender in this respect than birch or maple.

Cellulose Materials

Values for three cellulose materials are listed in the last three columns of table 1. It seems desirable, before discussing the values, to explain briefly the preparation and the nature of the cellulose materials.

Holocellulose is a solid wood residue prepared by removing the lignin by chlorinating the wood, and then dissolving the chlorinated lignin so formed with an ethanolamine-alcohol solution. The residue is a white, lignin-free fibrous cellulose product comprising practically all the cellulosic material in the wood. Alpha cellulose is the portion of holocellulose or any lignin-free cellulose material insoluble in 17.5 percent aqueous sodium hydroxide solution under specified conditions. Cross and Bevan cellulose is a white lignin-free cellulose fraction of wood obtained by chlorinating the wood and dissolving the chlorinated lignin with dilute aqueous sodium sulfite solution. In general, it comprises from 55 to 62 percent of the wood, depending on the species.

It may be noted in table 1 that aspen has 79.5 percent of holocellulose, 63.5 percent of Cross and Bevan cellulose, and 51.0 percent of alpha cellulose. These values are higher than the corresponding values from birch or maple. The results for the holocellulose and the Cross and Bevan cellulose show that aspen surpasses the other two species in holocellulose and Cross and Bevan cellulose on a weight basis. They suggest it should be a good source for refined chemical pulps for papers, and also for rayon and other cellulose derivatives, as indicated by the high alpha cellulose yield.

Aspen is a light wood, weighing 22 to 24 pounds per cubic foot on an oven-dry green-volume basis. Thus a cord of 85 cubic feet weighs less than an equal volume of some other wood. The weight of holocellulose, Cross and Bevan cellulose, and alpha cellulose in a cord of aspen, yellow birch, and sugar maple is recorded in table 2.

Table 2.--Percentage of cellulose in cord of wood on oven-dry green-volume basis

Species	Weight per cord	Cellulose per cord		
		Holocellulose	Cross and Bevan	Alpha
	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>	<u>Pounds</u>
Quaking aspen	1,870	1,486	1,187	953
Yellow birch	2,890	2,225	1,697	1,436
Sugar maple	2,970	2,233	1,793	1,485

Sapwood and Heartwood

Bigtooth aspen is also an important wood. It is similar to quaking aspen in structure, composition, and chemical and physical properties. Some valuable qualitative data on both the sapwood and the heartwood of this species are recorded in table 3 (4)2/. It may be noted that what has been said about the low lignin, the high Cross and Bevan cellulose, and the high holocellulose values of quaking aspen also applies to bigtooth aspen. The lignin content is 16.3 and 16.9 percent for the sapwood and the heartwood, respectively. The holocellulose yields are 78.0 percent for the sapwood and 80.0 percent for the heartwood. As may be noted in table 3, aspen compares favorably in composition with beech, yellow birch, paper birch, and sugar maple.

Further, aspen contains 80.0 percent of holocellulose, of which, on the wood basis, 22.5 percent is pentosans. This leaves 57.5 percent of the wood substance in aspen as hexosans. These hexosans, on hydrolysis, are converted to hexose sugars. Accordingly, aspen, even though it is a hardwood, should be a good source of wood sugar for fermentation to ethyl alcohol, conversion to molasses, or for propagation of fodder yeast.

Summative Components

In a rather complete analysis, as recorded in table 3, some overlapping of the values occurs. The cold-water extractives are also included in the hot-water extractives; methoxyl values are included in the lignin and the holocellulose values; and the pentosans and the acetyl values are included in the holocellulose. Wood can be divided into four component parts - extractives, ashes, lignin, and holocellulose. Thus a summative analysis of wood comprises determinations of the above four summative components (5) as recorded in table 4, in which are listed bigtooth aspen with beech, yellow birch, paper birch, and sugar maple.

2/ Underlined numbers in parentheses refer to Literature Cited at end of Part I of this report.

It may be noted that aspen is similar to the other four woods in that values of the four summative components are equivalent to approximately 100 percent of the oven-dry wood.

Composition of Cellulosic Fractions

A chemical analysis of aspen cellulose fractions showed that good quantitative data on the composition of the materials are obtainable (2). Thus, an analytical breakdown of the holocellulose and the Cross and Bevan cellulose according to the data in table 5 accounts for practically 100 percent of the two materials.

An analysis of wood sometimes comprises the determination of four cellulose fractions of the material (wood). They are (1) holocellulose, (2) Cross and Bevan cellulose, (3) hydrolyzed holocellulose, which is the residue remaining after holocellulose is hydrolyzed with 1.3 percent sulfuric acid for 2 hours, and (4) alpha cellulose. Differences in the degradation of these cellulose fractions can be determined by dispersing separately samples of each in a suitable solvent and measuring their viscosity. For example, samples from the least degraded dispersed cellulose fractions will flow most slowly from a viscometer tube.

In table 6 are recorded the yield and the viscosity (3) of holocellulose, Cross and Bevan cellulose, hydrolyzed holocellulose, and the alpha cellulose from each of the three fractions. As a means of comparison, the cellulose materials were prepared by the same procedure from quaking aspen, white spruce, red spruce, jack pine, balsam fir, and eastern hemlock, all commonly used as sources for pulps intended for papers.

It may be noted in table 6 that the values for the yield and the viscosity of the six cellulose fractions from the quaking aspen compare favorably with the yield and viscosity values for the corresponding cellulose fractions from the other five species. Aspen has 82.5 percent of holocellulose as compared with values ranging from 73.3 to 68.5 percent for the other five species. Aspen has 64.1 percent of Cross and Bevan cellulose as compared with yields ranging from 61.2 to 56.0 percent for the remaining woods. Aspen also leads the other five species in hydrolyzed holocellulose content with 63.7 percent as against values ranging from 61.0 to 55.3 percent from the other woods. It leads the other five woods in alpha cellulose yields from the holocellulose, the Cross and Bevan cellulose, and the hydrolyzed holocellulose, as may be noted in table 6.

Viscosity values are recorded in centipoises in table 6. Aspen holocellulose has a viscosity of 40.2 centipoises. Jack pine holocellulose has a viscosity of 50.1 centipoises. The holocellulose viscosities from the other four species range from 35.4 to 20.1 centipoises. Aspen Cross and Bevan cellulose has a viscosity of 28.9 centipoises, which is higher than the viscosity of the corresponding cellulose fraction from the other five woods.

Table 3.--Composition of American woods1/

Chemical composition	Bigtooth aspen		Beech		Sugar maple		Paper birch		Yellow birch	
	Sap-wood	Heart-wood	Sap-wood	Heart-wood	Sap-wood	Heart-wood	Sap-wood	Heart-wood	Sap-wood	Heart-wood
Ash	0.26	0.33	0.31	0.57	0.32	0.84	0.24	0.21	0.11	0.50
Solubility in:										
Cold water. . . .	2.70	1.36	2.33	.23	.81	.52	1.28	1.12	1.20	.93
Hot water	3.13	.99	2.17	.43	2.08	1.20	2.39	2.15	1.30	1.29
Alcohol-benzene .	2.41	2.13	1.37	.96	1.31	1.22	3.31	6.44	.97	1.89
Ether	1.02	1.03	.20	.57	.10	.89	.79	2.19	.36	.30
Acetyl.	5.48	6.07	7.13	6.05	6.56	4.94	7.12	7.60	8.79	6.11
Methoxyl.	5.27	5.35	6.28	6.44	6.34	6.50	6.10	5.75	6.01	6.04
Pentosan.	23.33	23.75	25.55	24.49	22.78	22.98	28.77	28.64	26.89	26.87
Lignin2/.	16.33	16.92	20.61	22.26	20.33	21.79	17.56	19.61	18.56	20.19
Cellulose	62.67	64.42	60.83	60.71	60.39	60.27	55.58	50.96	59.36	58.37
Cellulosan.	14.45	15.78	17.88	18.33	16.02	14.25	17.98	13.97	19.27	16.99
Holocellulose . . .	78.01	80.00	76.20	76.85	76.26	75.96	76.61	70.85	79.50	76.45
In holocellulose3/										
Acetyl.	5.17	5.05	5.15	4.76	5.12	4.05	6.01	5.29	6.13	5.81
Methoxyl.	.65	.72	.95	1.24	.83	.97	.97	.95	1.31	.93
Pentosan.	22.51	22.98	24.46	23.52	22.67	22.57	28.45	26.93	26.49	24.94

1/ Results in percentages of oven-dry (105° C.) wood.

2/ Ash-free.

3/ Percentage on original wood.

Table 4.--Composition of American woods,^{1/} summative analysis

Species	Ash	Solubility in		Lignin	Holocellulose	Total
		Hot water	Alcohol-benzene			
	Percent	Percent	Percent	Percent	Percent	Percent
Bigtooth aspen						
Sapwood. . .	0.26	3.13	2.41	16.33	78.01	100.14
Heartwood. .	.33	.99	2.13	16.92	80.00	100.37
Beech						
Sapwood. . .	.31	2.17	1.37	20.61	76.20	100.66
Heartwood. .	.57	.43	.96	22.26	76.85	101.07
Yellow birch						
Sapwood. . .	.11	1.30	.97	18.56	79.50	100.44
Heartwood. .	.50	1.29	1.89	20.19	76.45	100.32
Paper birch						
Sapwood. . .	.24	2.39	3.31	17.56	76.61	100.11
Heartwood. .	.21	2.15	6.44	19.61	70.85	99.26
Sugar maple						
Sapwood. . .	.32	2.08	1.31	20.33	76.26	100.30
Heartwood. .	.84	1.20	1.22	21.79	75.96	101.01

^{1/} Results in percentages of oven-dry (105° C.) wood.

Table 5.--Composition^{1/} of quaking aspen holocellulose and Cross and Bevan cellulose

Fractions and chemical groups	Holocellulose	Cross and Bevan cellulose
	Percent	Percent
Alpha cellulose..	61.4	76.3
Pentosans.....	26.7	19.9
Uronic acids.....	5.0	2.6
Acetyl.....	5.5	1.6
Methoxyl.....	1.1	.7
Totals.....	99.7	101.1

^{1/} Percentage values based on weight of oven-dry materials

Table 6.--Yield and viscosity of cellulosic materials from various woods/

Species	Holocellulose	Cross and Bevan cellulose	Hydrolyzed holo-cellulose	Alpha from -	
				Holo-cellulose	Hydrolyzed holocellulose
Quaking aspen:					
Yield.....	82.5	64.1	63.7	50.7	47.3
Viscosity.....	40.2	28.9	11.2	72.3	18.0
White spruce:					
Yield.....	73.3	61.2	61.0	49.5	43.7
Viscosity.....	32.7	17.2	13.7	68.2	21.1
Red spruce:					
Yield.....	72.9	60.3	60.5	48.3	43.3
Viscosity.....	35.4	18.8	11.6	56.7	18.4
Jack pine:					
Yield.....	72.5	58.3	59.1	49.5	43.1
Viscosity.....	50.1	26.9	15.8	77.7	21.1
Balsam fir:					
Yield.....	69.9	56.4	55.3	44.0	39.3
Viscosity.....	20.1	19.7	6.4	39.2	19.3
Eastern hemlock:					
Yield.....	68.5	56.0	55.4	48.2	41.7
Viscosity.....	23.0	20.3	8.5	36.1	20.9

1/ Percentage yield based on weight of oven-dry wood; viscosities expressed in centipoises in cuprammonium solution.

The viscosity of the alpha cellulose from aspen holocellulose is 72.3 centipoises. The corresponding value from jack pine is 77.7 centipoises; and the corresponding values from the two spruces, balsam fir, and eastern hemlock range from 68.2 to 36.1 centipoises. Aspen alpha from Cross and Bevan cellulose has a viscosity of 39.6 centipoises; it excels the viscosity of the corresponding cellulose fractions from the other five species.

These viscosity data indicate that aspen compares favorably in its resistance to the degradative effects of the chemical treatments involved in the preparation of the wood-cellulose fractions listed in table 6; aspen also should be a good source for cellulose fibers with good strength properties desirable for fabrication into yarns and films of various cellulose derivatives.

Aspen Holocellulose and Hemicellulose

Thomas (1) made a valuable contribution to the chemistry of aspen in his research on aspen holocellulose and hemicellulose. The latter is the material that dissolves when lignin-free cellulose is treated with a 17.5 percent aqueous sodium hydroxide solution. He prepared aspen holocellulose by chlorinating wood sawdust that was first slightly moistened with water and then suspended in carbon tetrachloride. The chlorinated sawdust was extracted with alcohol-monoethanolamine solution for the removal of the chlorinated lignin. The procedure avoided heating of the sawdust during chlorination, which occurs if the material is not suspended in a liquid for dissipating the heat generated during chlorination. It also reduced the possibility of degrading the holocellulose.

The yield of holocellulose on an ash-free basis was 77.5 percent. This high yield is another confirmation that aspen is a good potential source for cellulose, as stated earlier in this report. Thomas also carried on a rather extensive extraction operation for removing, stepwise, hemicelluloses from the holocellulose. The holocellulose was (a) given three 12-hour extraction treatments with cold water; (b) the residue was given three 4-hour extraction treatments with hot water; (c) the residue from the hot-water treatment was given two 2-hour extraction treatments with 5.0 percent potassium hydroxide; and (d) the residue from the 5.0 percent alkaline extraction was given two 1-hour treatments with 15.0 percent potassium hydroxide solution.

The filtrate from each of the above extractions was treated separately with alcohol to precipitate the hemicelluloses. Refining of the hemicelluloses was carried out by alternately dissolving and reprecipitating them with alcohol.

Yields

By the series of water and alkaline extractions about 27.0 percent of hemicelluloses was obtained from the aspen holocellulose, recorded in table 7 (values for fractions A to E, inclusive, in column (2)).

Calculated on the basis of the weight of the wood, the yield of the hemicellulose extracted was equivalent to about 20.8 percent (values for fractions A to E, inclusive, in column (3)).

Acetyl

The hemicelluloses A, B, and C in column (4) are shown to have between 8 and 9 percent acetyl groups which are undisturbed by the water extractions. On the other hand, acetyl is removed from the hemicelluloses by alkaline extractions, which accounts for the fact that no acetyl is shown in fractions D and E and in the cellulose residue. These results confirm the evidence that acetyl groups are associated largely with the hemicelluloses from aspen.

Methoxyl

Methoxyls, which on hydrolysis form methanol (wood alcohol), were associated with the various hemicellulose fractions to the extent of 2.34 to 2.48 percent, which confirms the modern concept that not all the methoxyl in wood is associated with the lignin.

Uronic Acids

Uronic acids comprised from 11.0 to 23.4 percent of the hemicellulose fractions.

Xylan and Glucosans

Except for fraction C, xylan comprises from 54.2 to 85.5 percent of the aspen hemicellulose fractions. No araban, also a pentose-forming material, was detected by Thomas. Glucosans in yields of 5.0 to 8.6 percent were present in the aspen hemicelluloses.

In general, the results of Thomas are in agreement with those of others who have worked on aspen. The low lignin and high cellulose content of the wood suggest the species to be a good hardwood source for cellulose in good yields, at moderate cost of chemicals required for delignification operations.

Aspen Cellulose Fibers

Cellulose fibers from aspen average approximately 1 mm. in length and their diameter is about $1/50$ mm. Delignified fibers from holocellulose comprise about 35.4 percent of hemicelluloses ($27.5/77.5 = 35.4$), and 64.6 percent of alpha cellulose ($100 - 35.4 = 64.6$). On the basis of the wood, the hemicellulose content is about 27.5 percent and that of alpha cellulose 50.0 percent. These values are the approximate potential yields of hemicelluloses and alpha cellulose. The value for hemicelluloses, however, is higher than that recovered from aspen holocellulose. So far the value of 20.8 percent (on the basis of the wood) obtained by Thomas appears to be the upper limit of hemicelluloses recovered from aspen holocellulose.

Table 7.--Yield and composition of aspen holocellulose and hemicellulose fractions

Fractions (1)	Yield1/ on basis of holocellu- lose (2)	Yield2/ on basis of wood (3)	Acetyl3/ (4)	Methoxy13/ (5)	Uronic3/ anhydride (6)	Xylan3/ (7)	Glucosans3/ (8)
	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Holocellulose	100.00	77.50	3.37	0.88	5.40	20.10	65.20
Hemicellulose A C.W.a/ 3.26		2.52	8.91	2.34	17.10	57.30	5.00
Hemicellulose B H.W.b/ 4.20		3.26	8.12	2.48	23.40	54.20	5.50
Hemicellulose C H.W.Ac/2.58		1.99	8.94	2.40	12.10	8.00	7.50
Hemicellulose D	11.30	8.75	0.00	1.70	14.60	82.70	8.60
Hemicellulose E	5.54	2.30	.00	1.70	11.00	85.50	7.90
Cellulose residue	65.30	50.60	.00	.15	.50	1.58	

1/ Yield of fractions on ash-free, lignin-free basis, calculated on weight of oven-dry holocellulose.

2/ Yields calculated on weight of extractive-free, oven-dry wood.

3/ Composition of fractions on ash-free, lignin-free basis calculated for oven-dry materials.

a/ Soluble in cold water.

b/ Soluble in hot water.

c/ Soluble in hot water and also alcohol; recovered by evaporation of alcohol.

Suggested Possible Chemical Uses for Aspen Wood

The composition of the delignified aspen fibers suggests that with further research they should be useful for the following purposes: (1) On account of their high hemicellulose content, they should be convertible to glassine-like and greaseproof papers with low power consumption. (2) Their high alpha cellulose content suggests that they would be a good source for materials intended for the manufacture of cellulose derivatives. (3) They should also be suitable for making high-yield bleached cellulose fibers for making white papers. (4) Their high hexosan material suggests that it should be possible to hydrolyze aspen carbohydrates to high yields of hexose sugars, most of which can be converted to ethanol by yeast fermentation. (5) The high holocellulose content suggests that aspen should be a good source of sugars for conversion to molasses or propagation of fodder yeast.

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CHEMICAL UTILIZATION OF ASPEN^{1/}

PART II: BARK

By

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Introduction

The chemical utilization of a forest crop in the production of the higher-grade papers and purified cellulose or high alpha pulp involves, in general, the problem of removal and disposal of the bark. This is particularly important in the case of aspen since the relatively small diameter of the tree reduces the ratio of wood to bark to the extent that as much as 15 to 20 percent of the harvested material may be bark. One of the controlling factors in the chemical utilization of aspen is the economic balance between cost of raw material and the recovery of salable product in the form of cellulose fiber. Under present methods of utilization in the higher-grade products, the cellulose fiber must bear the cost of removal and disposal of bark. This situation has been responsible for the economic idleness of large areas of smaller diameter second-growth aspen on the poorer sites, of which there are more than 3 million acres in Minnesota alone.

It is the purpose of this report to outline the present knowledge of the nature and chemical composition of aspen bark to aid in making it an asset rather than a liability. The information which is presented includes a discussion of the general characteristics of the bark and its chemical composition.

Characteristics of Aspen Bark

Aspen bark is notably variable in appearance from smooth and light colored to rough and dark. The normal bark is smooth and grey in color, with a powdery efflorescence consisting of sloughing periderm cells, and typically waxy in feel. The rough and darker colored bark is associated with abnormal periderm formation, apparently resulting from mechanical injury or attack by fungi and lichens (3).

The proportion of bark and its thickness as found on stems of various diameter classes from 1 to 11 inches is given in table 1 (4).

^{1/} Published as University of Minnesota Department of Agriculture Misc. Journal, Series No. 597.

Table 1.--Weight and thickness of aspen bark as related to tree diameter

Stem diameter	Average thickness	Average weight in percent of total weight of wood plus bark	
		Green	Oven-dry
<u>Inches</u>	<u>Inches</u>	<u>Percent</u>	<u>Percent</u>
1	.09	30.2	29.5
2	.12	22.6	23.2
3	.14	19.7	22.2
4	.19	19.2	21.9
5	.21	17.1	20.1
6	.23	15.4	17.9
7	.24	14.4	17.2
8	.29	14.7	17.0
9	.30	13.8	16.4
10	.37	13.5	15.8
11	.47	13.3	15.7

Morphologically (4), aspen bark is composed of four well-defined layers which may be observed in microscopic sections or may be easily separated by mechanical means. The outer layer or periderm normally consists of from six to eight rows of more or less rectangular cells (0.029 x 0.020 mm.) and makes up about 2 percent by weight of the dry bark. The second layer or cortex appears as a soft green mass of slightly tangentially elongated parenchyma cells (0.069 x 0.026 mm.) and makes up about 17 percent of the dry weight of the bark. The third and fourth layers compose the secondary phloem and together amount to about 81 percent of the bark. The third layer is composed of fibers (average length, 0.94 mm.) intermixed with stone cells (average length, 0.035 mm.), as well as ray cells and other parenchyma, and amounts to about 67 percent of the bark, while the fourth layer consists almost entirely of fibers (average length, 0.98 mm.), ray cells, and other parenchyma, and composes about 13 percent of the bark. The stone cells seem to be concentrated in relatively large numbers in the third layer or outer portion of the secondary phloem. Although sieve tubes are, of course, present in the secondary phloem, they do not survive the maceration or pulping technique employed in studying the cellular composition of the bark.

Chemical Composition of Aspen Bark

The methods and results of studies of the chemical composition of a large variety of barks have been summarized in reviews by Segall and Purves (6), and by Kurth (5). Although the literature through 1946 is well represented in these publications, no reference is made to the chemical composition of aspen bark. However, unpublished results of research carried on by Wangerin (7) at the University of Minnesota give a partial indication of the general chemical composition of the bark. A proximate analysis of aspen bark is given in table 2.

Table 2.--A proximate analysis of aspen bark

	<u>Bark</u>
Ash.....	4.05
Cold-water solubility.....	20.53
Hot-water solubility.....	23.06
Ether solubility.....	15.13*
Alcohol-benzene solubility.....	23.52
Lignin.....	23.86
Holocellulose.....	60.63
Cellulose.....	38.72
Pentosan.....	18.54

*Davenport (Michigan Conservation, p. 4-6, Dec. 1937) reports an ether solubility of 13.95 percent in an analysis of deer browse. Other analyses at the University of Minnesota indicate a value of 8-9 percent. The differences may well be due to seasonal variation.

Aspen bark is noteworthy in its high content of extractable material (4), as indicated in table 3, where it may be seen that about 36 percent of the bark is removed by extraction with organic solvents and water, and a further 8 to 10 percent is soluble in dilute ammonium hydroxide, as determined by the method of Anderson (1) for the extraction of pectic materials from wood. The latter is at present thought to be composed of pectins or other uronic acid containing carbohydrates. The organo-solvent extractives are composed of fatty materials and glucosides, while the water-soluble extractives appear to be composed of mono- and disaccharides, as well as other water-soluble higher polysaccharides.

Table 3 shows the extent of extractives obtained from various bark layers when each is extracted successively with the solvent series, including petroleum ether, ethyl ether, benzene, alcohol, and hot water.

Table 3.--Extraction of aspen bark^{1/}

Layer	Petroleum ether	Ether	Benzene	Alcohol	Hot water	Total ^{2/} organic extract	Total ^{3/} neutral extract	Pentosan in residue
Periderm	0.26	0.06	0.02	0.11	0.15	0.45	0.60	0.52
Second layer	2.56	.52	.22	5.45	4.55	8.75	13.30	2.35
Third layer	.71	1.14	.18	9.24	6.36	11.27	17.63	12.95
Inner layer	.35	.35	.07	2.25	1.83	3.02	4.85	1.98
Total	3.88	2.07	0.49	17.05	12.89	23.49	36.38	17.80

^{1/} Percent oven-dry weight of original whole bark.

^{2/} Successive extraction with petroleum ether, ether, benzene, and alcohol.

^{3/} Includes hot-water extract and total organic extract.

Calculations from these data show that 1.65 percent of the total extractive is found in the periderm, 36.5 percent in the second layer, 48.5 percent in the third layer, and 13.3 percent in the inner layer.

An analysis of the alcohol-benzene extract of aspen bark (²) indicates that about 90 percent of the extract is composed of phenolic glycosides along with a lipid fraction. The lipid fraction was found to consist of about 50 percent free fatty acid having an average chain length of 14 carbon atoms. The unsaponifiable portion amounted to about 25 percent of this fraction and was said to consist mainly of phytosterols, the latter being apparently responsible for the waxy appearance of the extract. The results are given in table 4.

Table 4.--Analysis of the alcohol-benzene extract
of aspen bark

	Percent
Volatile substance (100° C, in vacuo).....	10
Lipid substances.....	15
Phenolic glycoside	
Water-soluble.....	40
Water-insoluble.....	35
Nitrogen (Kjeldahl).....	0.06
Phosphorous.....	0.05
Pentoses.....	Trace
Fusion temperature.....	75° to 85° C.

Pulping Characteristics

Although the pulping properties of aspen bark have not been extensively investigated, it has been found (4) that the bark may be disintegrated by cooking with reagents such as sodium hydroxide or sodium sulfite. However, the pulp residue leaves much to be desired. In the case of alkaline cooking reagents, the pulp is exceedingly granular and appears to be composed of small balls of fiber associated with conglomerates of stone cells. The cellular components of the periderm and cortex as well as parenchyma and rays are lost in the screening, the residue consisting almost entirely of secondary phloem fiber and stone cells. In the case of a sodium sulfite cook, the bark largely retains its original form but on mechanical disintegration and screening, the secondary phloem is retained in a shredded and unpulped state. Microscopic examination shows the shredded material to be thin tangential sections of the secondary phloem composed of parenchyma and fibers, the ray cells and most of the stone cells having been removed. Yields and analyses of the pulps obtained by various cooking reagents are shown in table 5.

Table 5.--Pulping of aspen bark^{1/}

Reagent	Yield ^{2/}	Cellulose ^{3/}	Alpha Cellulose
	<u>Percent</u>	<u>Percent</u>	<u>Percent</u>
4 NaOH	26	79.1	73.5
8 Na ₂ SO ₃	43	71.1	

^{1/} Cook 2 hours at 160° C.

^{2/} Retained on Fourdrinier screen.

^{3/} Cross and Bevan.

Utilization

In the light of present knowledge of aspen bark, suggestions as to its possible utilization are, at most, extremely visionary. The yields and quality of fiber are not such as would encourage its use in any but low-grade fiber products. At present it is being used in the manufacture of wallboard where the nature of the product does not justify removal of the bark prior to pulping.

The mechanical separation of the inner fibrous layer of the bark from the outer nonfibrous materials appears to have possibilities and needs further investigation. Such separation might result in the production of a fiber from aspen bark that has possibilities in papermaking. A similar refining process is carried on with flax straw, in decorticating it for cigarette paper production.

If practical methods of recovery can be developed, the bark extractives appear to offer a possible source of chemical raw materials. However, the feasibility of such a method of utilization must await further information on the nature and composition of these extractives.

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